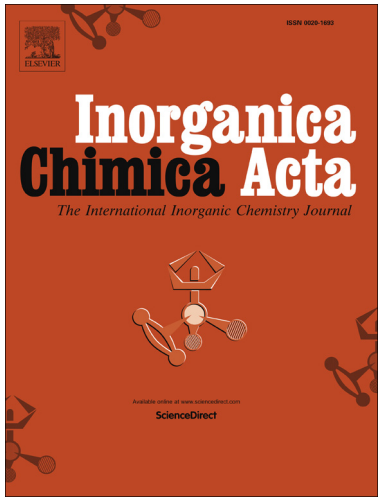

Review article

Malcolm L. H. Green: Reminiscences and Appreciations

John E. Bercaw, Jay A. Labinger

PII: S0020-1693(18)31906-6
DOI: https://doi.org/10.1016/j.ica.2018.12.044
Reference: ICA 18711

To appear in: *Inorganica Chimica Acta*

Received Date: 21 December 2018
Accepted Date: 24 December 2018

Please cite this article as: J.E. Bercaw, J.A. Labinger, Malcolm L. H. Green: Reminiscences and Appreciations, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.12.044

Malcolm L. H. Green: Reminiscences and Appreciations

John E. Bercaw[a] and Jay A. Labinger[a,b]
Division of Chemistry and Chemical Engineering[a] and Beckman Institute[b]
California Institute of Technology
Pasadena, CA 91125

We are greatly pleased to participate in this special issue of *Inorganica Chimica Acta* celebrating Malcolm Green. Having no new science worthy of the occasion to report (and feeling no great urge to recycle older work yet one more time), we offer instead a brief appreciation of Malcolm's contributions to inorganic chemistry, as well as what he has meant to us throughout our careers, both personally and professionally.

Malcolm was one of the earliest products of the Geoffrey Wilkinson school of organotransition metal chemistry, a group which, as one of us has documented [[1]], was a major factor in the mid-20th century "renaissance" of inorganic chemistry, in which Malcolm himself played no small part. Many of his early studies, both during his graduate student days and in his independent career at Oxford (following a brief sojourn at Cambridge), were focused on bent metallocenes and transition metal hydride complexes (often both): papers that had a significant influence on our own research programs. But even more importantly, his special ability to identify and delineate *patterns* of structure and reactivity was central to the transformation of organotransition metal chemistry, from a collection of interesting but poorly understood observations to the systematic and powerfully unified field it is today.

We can identify (at least) two of Malcolm's contributions that comprise key steps in the remarkable expansion of organotransition metal and inorganic chemistry during the second half of the 20th century. His 1968 monograph on the organometallic compounds of the transition elements [[2]] was the first full-length treatment to organize the field by ligand type rather than position of the metal in the periodic table, thereby avoiding a merely phenomenological collection of compounds and reactions in favor of a much more systematic presentation. It also paid close attention to mechanistic features, where information was available, particularly in the chapter on alkyl and aryl complexes ("one-electron ligands"), and concluded with a chapter on the role of organotransition metal complexes in catalysis. All of this was a direct antecedent to the way the subject is approached and taught today.

The second, of course, was "Covalent Bond Classification" (CBC), a universal scheme for formally describing, and relating to one another, essentially *all* transition metal compounds. This was first published in 1995 [[3]], although we (and everyone else in the field) had been hearing about the methodology and its evolution for some time whenever we crossed paths with Malcolm, at meetings or elsewhere. Its novel approach to organizing the field, basically abandoning the commonly-used concepts of oxidation state and coordination number, has become a widely (although by no means universally!) used tool, valuable both heuristically and pedagogically.

Among other noteworthy contributions with strong systematizing/explanatory power, we might also mention his 1977 paper delineating predictive rules for nucleophilic attack on π-ligands [[4]]. And not at all least, when we began our long-running collaborative project on C-H activation (in 1986), Malcolm's seminal work (which started at least as far back as the early 1970s [[5]]) played an important part in guiding our thoughts and approaches. Indeed, his later codification (with Maurice Brookhart) of C-H bond interactions with metal centers, in which the term "agostic" was introduced [[6]], helped lead to recognition of the crucial role of so-called sigma complexes in that and related chemistry.

We could go on at considerable length about the advances that can be credited to Malcolm's work — all we would need to do is excerpt from the reference lists we've given our students in the Organometallic Chemistry course we taught jointly for many years — but we won't; rather we'll proceed to some of our best personal memories of encounters with Malcolm.

Reminiscences: JAL

I learned about Malcolm as a force in the field shortly after starting my graduate work at Harvard (with John Osborn, another Wilkinson protégé) in 1968; the afore-mentioned book was a major help in shaping my understanding and planning my research program. To my great fortune (and Harvard's), Malcolm and Jenny came to spend a few months' sabbatical at Harvard during my last year (if I recall correctly, Harvard accommodated them in the extremely ritzy Beacon Hill neighborhood of Boston, a far cry from our grad student apartment), and I was able to spend a considerable amount of time with him discussing chemistry, especially experimental methodology: he showed me how to use the (then not very widespread in the field) Schlenk techniques. That wasn't needed for my Ph.D. project (on oxidative addition of Ir complexes), but proved invaluable for my subsequent postdoctoral (at Princeton) and independent (at Notre Dame) work, which was focused on much more air-sensitive organometallic complexes of the early transition metals.

Actually I learned not only about this careful and painstaking experimental approach, but also Malcolm's, shall I say, more heroic style. During my postdoc (with Jeffrey Schwartz) we were invited to serve as checkers for the preparation of Cp_2NbCl_2 that Malcolm's former student C. R. Lucas contributed to *Inorganic Syntheses* [[7]]. The preparation was on a 45-g scale, and the next-to-last step involved pouring a solution obtained by adding NaCp to $NbCl_5$ into a *liter* of concentrated HCl, heating to boiling, "carefully" adding 60 mL of liquid bromine (in portions) and boiling it off. The recipe appropriately included the phrase "Caution. Bromine attacks respiratory passages and should only be handled in an efficient hood," which of course I did; but there was a power failure right in the middle of that process: the hood motor shut down and I had to flee the lab. Fortunately both I and the experiment survived.

During the ensuing years my many encounters with Malcolm in various venues — meetings, my visits to Oxford, his visits to wherever I happened to be at the time (most

frequently after I came to Caltech in 1986) — were invariably intellectually stimulating and personally enjoyable. Two stand out in memory. First, a family trip through Europe (ahead of the 1979 ICOMC conference in Dijon) which took us through Oxford. Malcolm and Jenny entertained us at their recently-acquired farm in the Cotswolds; and then, when some other plans fell through and I found myself at loose ends for the last week before the conference, invited me to return to Oxford and stay with them. Every time I/we have passed through the area they have been similarly hospitable.

The second was the 1980 Gordon Conference on Organometallic Chemistry, which both John and I attended along with Malcolm. My records show that Malcolm gave a talk in a session on solar energy conversion, titled "Photoinduced Reaction of Some Transition Metal Hydrogen Compounds," which I must confess I do not recall at all (although I'm sure it was excellent). What I *do* remember is the drinking session on the Thursday evening, at which my partner-in-crime John Bradley and I recited limericks we had composed in "honor" of some of those present at the meeting. I can say without any undue modesty that the one we came up with for Malcolm was one of the all-time greats [[8]]. Unfortunately, like any good limerick, it is not appropriate for reprinting here; but Malcolm's response [[9]] was instantaneous, to the point, and at least as funny as the limerick itself.

Most of all, though, I remember — and treasure — our frequent discussions about chemistry, often spurred by one of Malcolm's new ideas about how features of inorganic chemistry could be explained, categorized, represented, *etc.* Many of them arose from applications of the CBC. I think I am inherently suspicious of what literary critics call "totalizing" theories — attempts to construct universally valid explanatory rubrics — whereas Malcolm seems to have been driven in that direction throughout his career. But such disagreements were (for me at least) extremely valuable in sharpening my understanding: the search for counterexamples and counterarguments always spurred me to think of things in new ways, whether we ended by agreeing or, more often, agreeing to disagree.

The most recent such encounter — in print, not in person — was initiated by a review article jointly written by Malcolm, Jenny and Ged Parkin [[10]], in which they proclaimed (among other things) that the long-standing convention of drawing the so-called Fp dimer, $[CpFe(CO)_2]_2$, with an Fe-Fe bond, was in fact a misrepresentation. I felt certain they were wrong — not necessarily that their representation of choice and arguments for it were flawed, but rather that virtually *any* such a categorical claim for a preference that could apply under all circumstances was not sustainable. Trying to justify that feeling, first to myself and then to others, led me to reflect on the analogy between chemical structure representation and literary translation, eventually resulting in a paper [[11]] in an earlier *Festschrift* issue of this journal (that one was for Al Cotton), and constituting a significant component of my ongoing project on connections between science and literature. I'm not sure whether my paper did much (anything?) to shake Malcolm's convictions, but he did graciously (as always!) compliment the writing style.

Reminiscences: JEB

The first time that I learned Malcolm Green was an accomplished organometallic chemist was as a young graduate student beginning my thesis projects with (an also young) Hans Brintzinger, then an Assistant Professor of Chemistry at the University of Michigan. Having no experience with organotransition metal chemistry, I went to the library and read Malcolm's monograph [2]. I have been fascinated by the subject ever since. I believe that the first time I actually *met* Malcolm was at the 1978 meeting of the American Chemical Society in Miami, at which my then colleague, Bob Bergman, and I each organized back-to-back two day symposia on organotransition metal chemistry. We invited Malcolm (and Jay) to speak. My symposium was focused on organometallic chemistry of the early transition metals. I convinced an artist friend, John Kimball, to prepare a cartoon (Figure 1) to commemorate the occasion. You can see Malcolm on the far left leading his mule carrying some of his molybdenocene and tungstenocene derivatives. Malcolm is telling the rest of us to keep moving west in the Periodic Table to groups 3-5. I had been an independent academic at Caltech for about six years by then, and Bob and I had jointly introduced and taught several times a course on organotransition metal chemistry to Caltech students. Bob and I were forced to put our lectures together primarily using journal articles. We were influenced strongly by Malcolm's publications as well as his book.

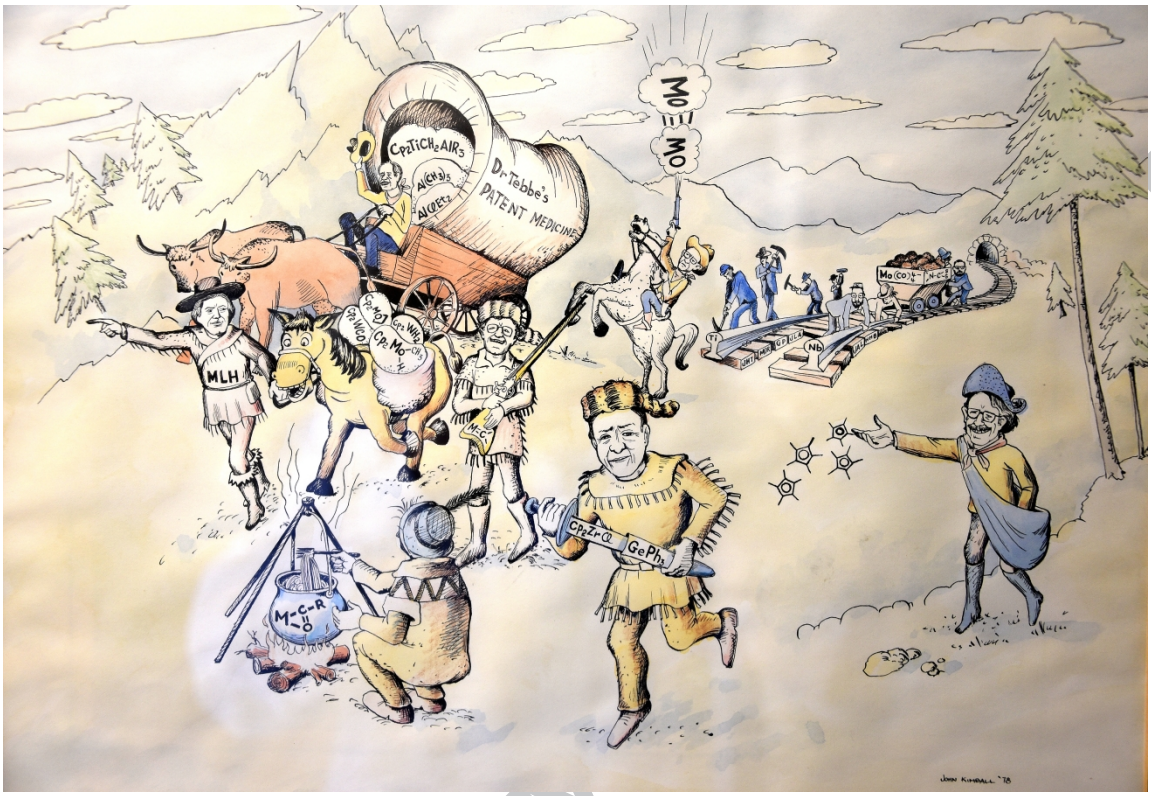

Figure 1. Cartoon showing participants of the symposium on Organometallic Chemistry of the Early Transition Metals at the 1978 ACS National Meeting. From left to right in front: Malcolm Green with mule, Fred Tebbe riding in covered wagon, Dick Schrock carrying his metal carbene (*sic*), Michael Lappert, John Bercaw (aka Johnny Appleseed) spreading his Cp*'s as he goes west. Further back: Al Cotton on horse, Jay Labinger laying the Nb rail, John Ellis in far rear pushing mining cart. The squatting person in front cooking spaghetti is intended to be Carlo Floriani (no facial picture was available to artist John Kimball).

Soon after the Miami ACS meeting, as Jay mentioned (*vide supra*), Malcolm and I attended the 1980 Gordon Research Conference on Organometallic Chemistry, where we became good friends. It was there that I was introduced to Malcolm's style when attending conferences. When he speaks he periodically stares up to the heavens, presumably seeking some divine insights into the subject at hand. When in the audience he passes notes to those nearby with drawings of organotransition metal compounds or of reactions sketched out. He includes a short quiz for the recipient with seemingly simple questions: "what is the electron count, coordination number, or valency for the metal?", "what do you predict for the product of the reaction?". Malcolm delighted in reading answers, especially when it was obvious that some education by him was in order.

In 1981 Malcolm and his family came to Caltech for a few months; Malcolm was one of the earliest (and most successful) of our Sherman Fairchild Visiting Scholars (see Figure 2). Malcolm and Jenny threw themselves into the department completely by engaging

with several groups. Jenny carried out some experiments with graduate student Christine McDade probing the mechanism for thermal decomposition of $Cp^*_2Ti(CH_3)_2$ to $Cp^*(C_5Me_4CH_2)TiCH_3$; they implicated an intramolecular α-abstraction leading to methane and a $[Cp^*_2Ti{=}CH_2]$ species that then rearranges to the final product. The paper that appeared in *Organometallics* [12] has now been cited over 200 times. Malcolm spent his time developing and promoting his MLX scheme for electron counting. I was soon a believer and began teaching his formalisms to students in my intermediate inorganic chemistry classes. When approached by a visitor to the department who inquired what were his duties as a Fairchild Visiting Scholar, Malcolm usually replied that there were no formal duties, but the informal ones were killing him!

Figure 2. Photo of Malcolm, Jenny, and daughter Sophie, at the home of the author (JEB) during their stay at Caltech in 1981.

In 1989 Malcolm reciprocated by inviting me to visit Oxford as a Guest Research Fellow. I was there for about 4 months; my wife Diane and daughter Karin joined me for the first 2 months. Malcolm and Jenny were superb hosts. They arranged a flat for us in Summertown on Mayfield Road. Each day I would enjoy the stroll to the Inorganic Chemistry Laboratory down Banbury Road. On some Sunday afternoons Malcolm would stop by with a couple of pints following a day of plumbing and electrical work as part of the renovation of the newly purchased house on Blandford Avenue.

This time at Oxford was my only real sabbatical while at Caltech, and I could not have chosen a better place. Whereas I did not go into the lab during that period, I greatly enjoyed discussing chemistry with Malcolm and my office mate, Ernesto Carmona, visiting from Sevilla, as well as others at the ICL. Philip Mountford was extremely patient and helpful in showing me around and in connecting me with my research group daily by the primitive Internet of that time. Malcolm, Ernesto, and I had regular lunches where we discussed chemistry and life more generally. For these outings he usually greeted us at his office holding a pipe that he used more like a teething ring than a smoking device. The mouthpiece was badly chewed and splintered, and he tapped the bowl with his right index finger, even when lit, so that the tip of his finger was scarred and black. Given his animated style of speaking about chemistry, the black soon covered much of his face and hands.

I spent much of the time at Oxford learning about olefin polymerization catalysis, a relatively new area of research for my group at Caltech. It was my good fortune that a graduate student of Malcolm's at the time was "Nobu" Ishihara from Idemitsu. He had made a very impactful discovery in polystyrene catalysis, and Idemitsu rewarded him by allowing him to pursue his PhD with anyone…he wisely picked Malcolm. Nobu endured my enthusiastic questioning about Ziegler-Natta polymerization. After several such sessions over tea in the Abbot's kitchen, a group of Malcolm's students approached me to explain that Nobu was very distraught, and that he was concerned that I did not like his answers to my (aggressive sounding) questions. I immediately approached Nobu to explain that I greatly valued these discussions, and that I was just excited. Fortunately, Nobu was relieved and understood. Over the next months he taught me a great deal about olefin polymerization, and we became great friends.

I have some vivid memories of the research labs in the ICL. There were group cleanups during which Malcolm would sit on a stool in front of a fume cupboard disposing of old pyrophoric chemicals — often by a (mostly) controlled burning. There was the view from the hallway of the enormous MVS instrument, constructed earlier by Geoff Cloke, that consumed massive amounts of liquid nitrogen when operating, then required cleaning afterwards, usually by a young student who was sent into the open end of the lifted metal bell jar armed with a box of Kimwipes and a squirt bottle of methylene chloride, scrubbing away until the fumes nearly overcame him.

In the ensuing years Malcolm and I travelled to the same meetings and met several other times at Caltech or Oxford. We exchanged students, notably Mark Thompson, Ged Parkin, and Vernon Gibson. We published several papers together. My admiration for him grew, as did my affection. One of his outstanding characteristics is his ability to properly mentor scientists, not only his own students and postdoctoral fellows, but others as well. He actively seeks out younger chemists at meetings and generously gives encouragement to them while entertaining them all the while. Malcolm Green's enthusiasm is clearly contagious. Malcolm makes doing chemistry truly fun!

References

References

[1] [ ] J. A. Labinger, Up from Generality: How Inorganic Chemistry Finally Became a Respectable Field, Springer, Dordrecht, 2013.

[10] [ ] J. C. Green, M. L. H. Green, G. Parkin, The Occurrence and Representation of Three-Centre Two-Electron Bonds in Covalent Inorganic Compounds, Chem. Commun., 48 (2012) 11481-11503.

[11] [ ] J. A. Labinger, Does Cyclopentadienyl Iron Dicarbonyl Dimer Have a Metal-Metal Bond? Who's Asking?, Inorg. Chim. Acta, 424 (2014) 14-19.

[12] C. McDade, J. C. Green, J. E. Bercaw, A Kinetic and Mechanistic Study of the Thermolysis of Bis(pentamethylcyclopentadienyl)dimethyltitanium(IV), Organometallics, 1 (1982) 1629-1634.

[2] [ ] M. L. H. Green, Organometallic Compounds. Volume Two: The Transition Elements, Methuen & Co., London, 1968.

[3] [ ] M. L. H. Green, A New Approach to the Formal Classification of Covalent Compounds of the Elements, J. Organometal. Chem., 500 (1995) 127-148.

[4] [ ] S. G. Davies, M. L. H. Green, D. M. P. Mingos, Rules for Predicting Regioselectivity of Nucleophilic Attack on 18-Electron Organotransition Metal Cations Containing Polyene Ligands, Nouv. J. Chim., 1 (1977) 445-447.

[5] [ ] M. Brookhart and M. L. H. Green, Carbon-Hydrogen-Transition Metal Bonds, J. Organometal. Chem., 250 (1983) 395-408.

[6] [ ] M. L. H. Green, P. J. Knowles, Formation of a Tungsten Phenyl Hydride Derivative from Benzene, Chem. Commun., (1970) 1677.

[7] [ ] C. R. Lucas, J. A. Labinger and J. Schwartz, Inorg. Synth., 28 (1990) 267-270.

[8] [ ] To be fair, "Green" is relatively easy to rhyme — unlike, say, Bercaw — although we did manage that one too.

[9] [ ] That *was* printable; it will be fairly meaningless in the absence of what preceded it, but for the record I'll give it anyway: "Yes, and I've got the only one big enough to do the job!"